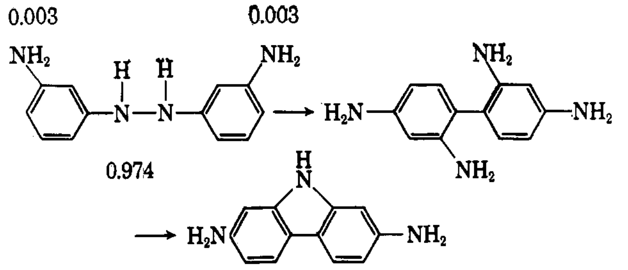
"π-complex" would have to lead to the formation of a second intermediate which would undergo transformation in the rate-determining step of the reaction. If the rearrangement of HzA proceeds by the same reaction sequence as the rearrangement of hydrazobenzene, the attack of proton on the "π-complex" would have to result in the formation of a second intermediate. A very likely candidate for the second intermediate would be a pair of cation radicals.

Observation that oxidation of diphenylamine,[21] α-naphthylamine,[22] and N,N-dimethylaniline[23] in acid solution leads to the formation of the corresponding substituted benzidines lends support to the proposed radical intermediate. As further evidence Hammond and Seidel[24] have observed that production of N,N'-diphenylbenzidine by acid-catalyzed rearrangement of tetraphenyltetrazine is accompanied by formation of by-products suggestive of the involvement of free radicals.

The probability that two positively charged cation radicals could form a "π-complex" might at first seem to be quite low; however, Hausser[25] has presented evidence that the Würster cation (the positively charged radical obtained by oxidation of N,N,N',N'-tetramethyl-p-phenylenediamine) can exist in such a form. The results of Hammond and Neuman[11] show that geminate recombination of pairs of cation radicals can be rather significant.

Appendix

Calculation of the amount of *ortho* coupling took into account the N^{15} that appeared in amino groups during reduction of *m*-nitroaniline. Since there are three coupling processes, *para–para*, *ortho–ortho*, and *ortho–para*, there is insufficient data to allow complete analysis of the problem; *e.g.*, a *para* coupling fraction of 0.5 could arise from either *ortho–para* coupling or from equal amounts of the other two processes. The following example, involving HzA from synthesis A, illustrates the method of calculation.



$$z = (0.974 + 0.003)x + \left(\frac{0.974}{2} + 0.006\right)y$$

where $x =$ *para* coupling fraction, $y =$ *ortho* coupling fraction, $z =$ number of nitrogen atoms per molecule of 2,7-diaminocarbazole, and $x + y = 1$.

Acknowledgment.—We are grateful to Professor James N. Pitts and to the University of California at Riverside for the use of the mass spectrometer. The work was partially supported by the National Science Foundation.

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[21] H. Wieland, *Ber.*, **46**, 3296 (1913).

[22] Reverdin and de la Harpe, *Chemiker-Ztg.*, **16**, 1687; Beilstein, "Handbuch der Organische Chemie," Vol. 12, Springer, Berlin, 1929, p. 1213.

[23] W. Michler and S. Pattinson, *Ber.*, **14**, 2161 (1881).

[24] G. S. Hammond, B. Seidel, and R. E. Pincock, *J. Org. Chem.*, **28**, 3275 (1963).

[25] K. H. Hausser and J. N. Murrell, *J. Chem. Phys.*, **27**, 500 (1957).

Mechanisms of Photochemical Reactions in Solution. XVI.[1] Photosensitized Dimerization of Conjugated Dienes

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Received May 27, 1963

Conjugated dienes are dimerized by irradiation in the presence of various photosensitizers. Structural assignments have been made to the dimers of 1,3-butadiene, isoprene, and cyclopentadiene. Preliminary studies of the dimerization of the piperylenes and 2,3-dimethyl-1,3-butadiene have been made. Formally, all of the observed products are consistent with the addition of triplet diene to another molecule to form diallylic biradicals.

Photosensitized irradiation of 1,3-butadiene,[3] cyclopentadiene,[4] and isoprene[5] has been reported in preliminary form. This paper relates some details of these and related reactions with emphasis on assignment of structures of the products. Preliminary discussion of mechanistic considerations have appeared elsewhere.[3-5]

Results

Photosensitized dimerizations of conjugated dienes were carried out by irradiation of solutions or neat liquid dienes containing various carbonyl compounds. Different sensitizers gave products in varying relative amounts in some cases, but there was no instance in which a product formed in the presence of any one sensitizer was absent from the product mixture formed in the presence of another sensitizer. Reactions were run both on a preparative scale and in degassed, sealed tubes. The two procedures gave no detectable differences in product distributions.

1,3-Butadiene.—These products, **1**, **2**, and **3** are produced from the photosensitized dimerization of butadiene.[3] *trans*-1,2-Divinylcyclobutane (**1**) is the major product in most experiments. The *cis* isomer, **2**, is formed in small amounts in all experiments, while the amount of 4-vinylcyclohexene (**3**) varies from 43% to 2%. The composition of the product mixtures depends strongly on the sensitizer employed.[3,5]

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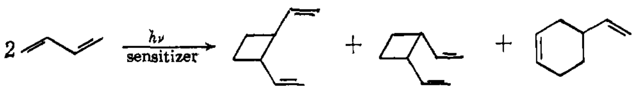
[1] Part XV: G. S. Hammond and W. M. Hardham, *Proc. Chem. Soc.*, 63 (1963).

[2] (a) National Science Foundation Predoctoral Fellow, 1960-1963; (b) Du Pont Summer Fellow, 1962; Woodrow Wilson Summer Fellow, 1963.

[3] G. S. Hammond, N. J. Turro, and A. Fischer, *J. Am. Chem. Soc.*, **83** 4674 (1961).

[4] N. J. Turro and G. S. Hammond, *ibid.*, **84**, 2841 (1962).

[5] G. S. Hammond and R. S. H. Liu, *ibid.*, **85**, 477 (1963).



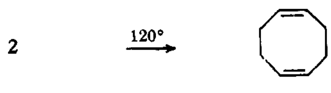
1 **2** **3**

The physical constants and infrared spectra of the three photodimers agree exactly with those reported in the literature.[6,7]

The nuclear magnetic resonance spectrum (n.m.r.) of **1** consists of resonances at 5.9 to 5.3 p.p.m.[8] and a series of overlapping doublets from 4.80 to 4.50 p.p.m. due to a total of six vinyl protons, a broad band centered at 2.4 p.p.m. due to two tertiary allylic protons, and a multiplet at 1.6 p.p.m. due to four methylene protons. Ozonolysis of **1** produces *trans*-cyclobutane-1,2-dicarboxylic acid.

The n.m.r. spectrum of **2** consists of resonances at 6.20 to 5.30 p.p.m. and 5.00 to 4.50 p.p.m. due to six vinyl protons, at 3.00 to 2.50 p.p.m. due to two tertiary allylic protons, and at 2.0 to 1.3 p.p.m. due to four methylene ring protons. Compound **2** undergoes smooth rearrangement at 120° to *cis,cis*-1,5-cyclooctadiene,[7] which was identical with authentic material.

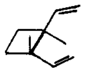
Compound **3** is identical in all respects with an authentic sample of 4-vinylcyclohexene.



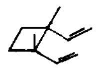
Isoprene.—Photosensitized dimerization of isoprene leads to the formation of seven products, **4, 5, 6, 7, 8, 9,** and **10**. An eighth photoproduct may have been formed but never amounted to as much as 1% of the mixture of dimers. Structural assignment was complicated by the fact that still another dimer, **11,** is formed by thermal isomerization of **5** during distillation and if the inlet temperature was too high, during vapor chromatography. Rearrangement of **5** gives **8, 9,** and **11.** Rearrangement of **4** to **7** and **10** also was observed. Pure or nearly pure samples of the seven photoproducts and the products of thermal rearrangements were obtained by preparative vapor chromatography. Structural assigments have been made, largely on the basis of n.m.r. spectra.

Eighteen cyclodimers of isoprene can be formulated. Structures may be grouped as twelve cyclobutanes, four cyclohexenes, and two cyclooctadienes. All of the cyclobutanes contain two terminal vinyl protons ($\mathrm{CH_2{=}C}$) plus zero–two other vinyl protons. The cyclohexenes contain each only one vinyl group, one or two other vinyl protons, two allylic and one nonallylic methylene groups. The cyclooctadienes contain no vinyl groups. These key features, which are reflected in the n.m.r. spectra, lead to rapid reduction of the problem of structure assignment.

The n.m.r. spectrum of **4** shows (1) a symmetrical band at 0.9 p.p.m., (2) a complex group having at least fourteen peaks between 1.0 and 2.4 p.p.m., (3) a group of peaks between 4.5 and 4.9 p.p.m., and (4) a group of six peaks with some substructure between 5.4 and 5.9 p.p.m. The integrals of the areas under the curve are in the ratio 3.03:2.25:2.04:1.00. The resonances are assigned, respectively, to two equivalent methyl groups, two methylene groups, two $\mathrm{{=}CH_2}$ groups, and two other ethylenic protons. Obviously, the compound is a dimethyldivinylcyclobutane. The two stereoisomeric 1,3-dimethyl-1,3-divinylcyclobutanes can be eliminated as possible structures as in both structures one would not expect strong coupling of the methylene protons with any other protons in the molecule; so the resonance should be that of two equivalent A_2 groups for the *trans* isomer and of two AB groups for the *cis* isomer. On the other hand the methylene protons in *cis*- or *trans*-1,2-dimethyl-1,2-divinylcyclobutane (structure **4a** and **4**) should be an A_2B_2 group which could account for the complexity of the spectrum of methylene protons. Furthermore, the fact that the compound readily undergoes rearrangement to a cyclohexene and a cyclooctadiene essentially eliminates the two 1,1,3,3-substituted structures.



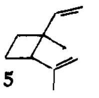
4



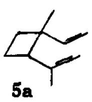
4a

A choice between **4** and **4a** can only be made tentatively. However, we believe that the assigned structure of **4** is correct for two reasons. First, *trans* compounds, but not always *cis* isomers, have been formed in each of the 1,2–1,2 cycloadditions that we have studied thus far. Second, thermal rearrangement of **4** gives a mixture of two compounds, which is in agreement with the recent observation[9,10] that *trans*-1,2-divinylcyclobutane rearranges to vinylcyclohexene and 1,5-cyclooctadiene at high temperature, whereas *cis*-1,2-divinylcyclobutane[7] is known to rearrange only to 1,5-cyclooctadiene.[11]

The n.m.r. spectrum of **5** shows (1) a single peak attributed to a methyl group at 0.9 p.p.m., (2) a complex group of peaks between 1.0 and 2.2 p.p.m. attributed to four methylene groups and a sharp peak at 1.4 p.p.m. attributed to an allylic methyl group, (3) a complex group of lines due to four protons, in two $\mathrm{{=}CH_2}$ groups, between 4.3 and 4.8 p.p.m., and (4) an unsymmetrical quartet between 5.5 and 6.1 p.p.m. assigned to a single, nonterminal vinyl proton. Integration is consistent with the assignments. Repetition of the arguments presented previously leads to the assignment of the structure of **5** in preference to **5a**.



5



5a

The n.m.r. spectrum of **6** shows (1) a broad group of peaks between 1.65 and 2.5 p.p.m. (relative area, 10.0) assigned to two methyl groups containing allylic protons and four methylene protons, (2) a group of peaks between 2.5 and 2.9 p.p.m. (relative area, 2.00) assigned to two tertiary protons attached to the cyclobutane ring, and (3) a peak at 4.7 p.p.m. (relative area 3.6) assigned to two $\mathrm{{=}CH_2}$ groups. Since the compound is considerably more thermally stable than *cis*-

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(6) W. H. B. Reed, *J. Chem. Soc.*, 685 (1951).

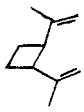
(7) E. Vogel, *Ann.*, **615**, 1 (1958).

(8) All n.m.r. resonances reported here are relative to an external sample of tetramethylsilane at 60 Mc., unless specified.

(9) F. A. L. Anet and J. S. Hartman, *J. Am. Chem. Soc.*, **85**, 1204 (1963).

(10) G. S. Hammond and C. DeBoer, unpublished results which show that rearrangement does not involve cracking to butadiene as has been previously assumed.[7,9]

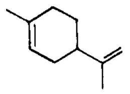
(11) The mechanistic implications of these observations will be developed elsewhere.



6

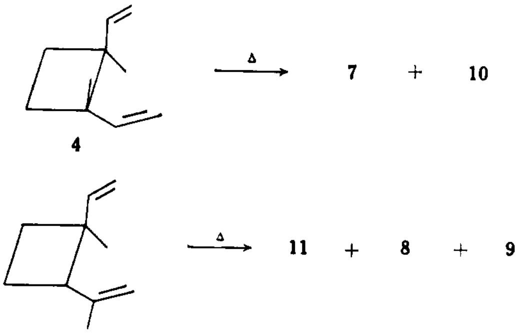
1,2-divinylcyclobutane it is assigned the structure of *trans*-1,2-diisopropenylcyclobutane.

Compounds **7**, **8**, and **11** are derivatives of cyclohexene since their n.m.r. spectra indicate the presence of one $=CH_2$ group, one ring vinyl proton, and in some cases another vinyl proton. Compound **8** was readily identified by comparison with *d,l*-limonene.



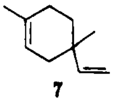
8

Comparison of compounds **7** and **11** with the cyclohexene derivatives obtained by thermal dimerization of isoprene is helpful since partial structural assignments have been made to those products. Early work recently has been reviewed briefly by Walling and Peisach.[12] All authors seem to agree that *d,l*-limonene is a major product. Walling and Peisach considered that the material boiling at 95.0–95.8° (60 mm.) was an inseparable mixture of limonene and 2-methyl-4-isopropenylcyclohexene since dehydrogenation and oxidation of the sample gave a mixture of phthalic and isophthalic acids. This result is confirmed by Binder, *et al.*,[13] who separated the fraction by extraction with silver nitrate. A lower boiling fraction was considered to be pure 2,4-dimethyl-4-vinylcyclohexene by Binder, *et al.*, although chemical degradation had convinced Walling and Peisach that the material was a mixture. Comparison of the infrared spectrum reported for this fraction by Binder, *et al.*, with ours shows it to be a mixture of **7** and **11**. The n.m.r. spectra of both compounds show the presence of vinyl groups (ABC pattern between 4.4 and 5.9 p.p.m.) along with one additional vinyl proton. The other spectral features are also compatible with assignment of the structures of the two compounds as 1,4-dimethyl-4-vinylcyclohexene and 2,4-dimethyl-4-vinylcyclohexene as has been done by Walling and Peisach[12]; however, the spectra are no help in deciding which compound has which structure. A reasonable grounds for decision can be found in consideration of the rearrangement reaction of the cyclobutanes, compounds **4** and **5**.

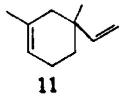


5

Although discussion of the detailed mechanisms of these rearrangements will be deferred, we have considered no mechanisms which do not involve (1) breaking the bond joining the two allylic systems, and (2) formation of a new bond involving two of the four termini of the allylic moieties.[14] Compounds **9** and **10** are cyclooctadienes (*vide infra*). Subject to the restrictions stated, only one other product, 1,4-dimethyl-4-vinylcyclohexene, can be formed from **4**, whereas two other products, *d,l*-limonene and 2,4-dimethyl-4-vinylcyclohexene, are formed from **5**. This line of reasoning leads to assignment of the following structures.

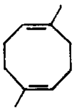


7

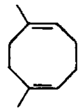


11

The mixture of **9** and **10** was never completely separated by preparative v.p.c. procedures, but sufficient fractionation was obtained to determine that **9** has an infrared absorption band at 9.35 μ and **10** has a band at 9.15 μ. The n.m.r. spectra of mixtures of the compounds show the presence of only two vinyl protons as judged by the relative areas under the traces between 1.5 and 1.9 p.p.m. (six methyl protons) and those between 5.0 and 5.5 p.p.m. (two vinyl protons). Reiteration of the reasoning (*vide supra*) leading to differentiation between **7** and **11** leads to the following structural assignments.



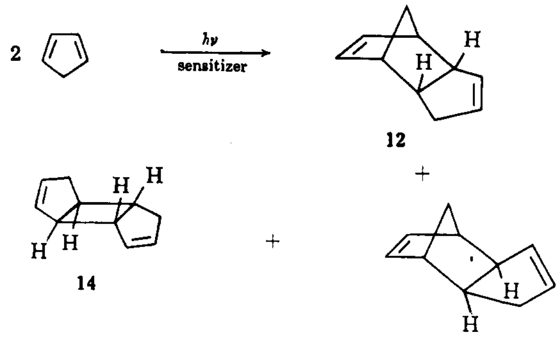
9



10

The use of different sensitizers leads to extreme variation in the relative amounts of the various products.[5]

Cyclopentadiene.—Photosensitized dimerization of cyclopentadiene[4] proceeds according to the following equation.



The three dimers are produced in approximately equal amounts (after correction for the thermal dimerization) irrespective of the sensitizer employed.

Compound **12** is *endo*-dicyclopentadiene, the common thermal dimer; **13** is identical with an authentic sample of *exo*-dicyclopentadiene prepared by the method of Bartlett and Goldstein.[15]

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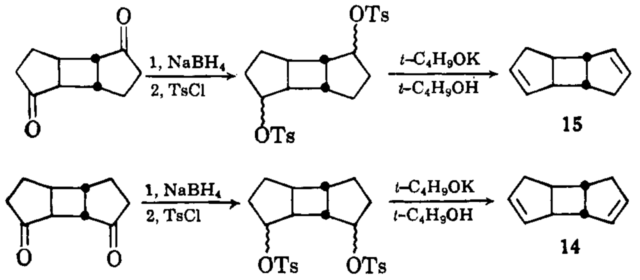
[12] C. Walling and J. Peisach, *J. Am. Chem. Soc.*, **80**, 5819 (1958).

[13] J. L. Binder, K. C. Eberly, and G. E. P. Smith, Jr., *J. Polymer Sci.*, **38**, 229 (1959).

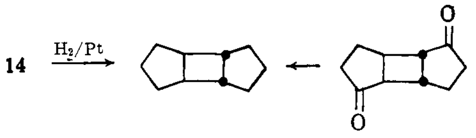
[14] Note that this statement, which is the minimum required for assignment of structures to compounds **7** and **11**, is independent of the tentative assignment of stereochemistry to **4** and **5**.

[15] P. D. Bartlett and I. S. Goldstein, *J. Am. Chem. Soc.*, **69**, 2553 (1947).

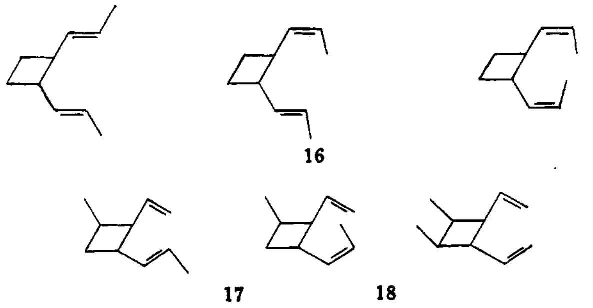
The n.m.r. spectrum of **14** features a sharp peak due to four vinyl protons at 5.70 p.p.m.; a broad band centered at 3.0 p.p.m. due to two tertiary allylic protons; and a pair of overlapping doublets at 2.45, 2.65, and 2.90 p.p.m. due to six methylene ring protons. The infrared spectrum of **14** is very similar to that of cyclopentene. It seemed likely that the compound was one of the isomers of tricyclo[5.3.0.0^{2,6}]decadiene. The location of the double bonds and the stereochemistry of **14** was demonstrated by reference to the photodimers of 2-cyclopentenone whose structures have been proven by Eaton.[16] The following transformations were carried out.



The sample of **14** prepared by the preceding procedure is identical with the photodimer. Furthermore, **15** could be separated from **14** by v.p.c., which showed that the photoproduct was uncontaminated with isomeric material. Catalytic hydrogenation of **14** produces a hydrocarbon identical with that obtained by the Wolff-Kischner reduction of *cis,trans,cis*-tricyclo[5.3.0.0^{2,6}]deca-3 8-dione.[16]



Piperylenes.—Mixtures of *cis*- and *trans*-piperylene containing sensitizers (benzophenone, benzil, or 2-acetonaphthone) were irradiated. Vapor chromatographs indicated the presence of at least 15 dimers in product mixture. Three products (**16, 17,** and **18**) were predominant. They have been isolated by preparative vapor phase chromatography. By analogy to other dimerization reactions and from consideration of their n.m.r. spectra, the gross structures of the three compounds have been tentatively assigned as *trans*-1,2-dipropenylcyclobutane(s),[17] **16**; 1-methyl-*trans*-2-vinyl-3-propenylcyclobutane, **17**; and 1,2-dimethyl-*trans*-3,4-divinylcyclobutane, **18**. The composition of product mixtures varies as the sensitizer is varied.



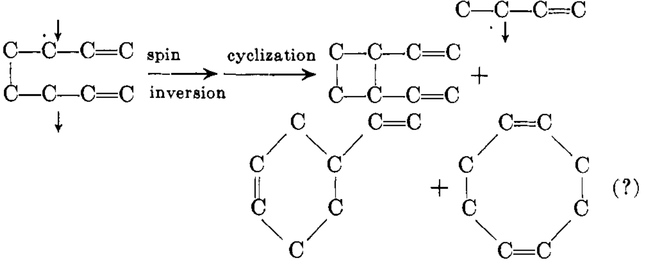
2,3-Dimethyl-1,3-butadiene.—Solutions of various sensitizers (six ketones) in the diene were irradiated. All product mixtures contained seven dimers which have not yet been separated and characterized. The composition of the product mixtures depends on the sensitizer used.

Discussion

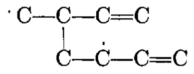
The structural assignments are all consistent with the following mechanism[3,4] for photosensitized dimerization of conjugated dienes (S is a photosensitizer).

$$\mathrm{S} \xrightarrow{h\nu} \underset{\text{excited singlet}}{\mathrm{S}^{*(1)}} \longrightarrow \underset{\text{triplet}}{\mathrm{S}^{*(3)}}$$

$$\mathrm{S}^{*(3)} + \mathrm{C{=}C{-}C{=}C} \longrightarrow \mathrm{S} + \mathrm{C{=}C{-}C{=}C}^{*(3)}$$



None of the observed products require that one-half of any intermediate possess a nonallylic structure.



not formed

The fact that cyclooctadienes are formed from isoprene suggests that terminal coupling of the biradicals may occur. However, it should be noted that no derivatives having *cis*-dialkenyl structures are produced. It is entirely possible that such compounds are formed but rearrange to cyclooctadienes during the work-up procedure. Such a hypothesis would account for the apparent contrast between the results obtained with isoprene and with butadiene.

Variation in the relative amounts of products formed from the acyclic dienes in the presence of different sensitizers has been attributed[5] to production of *cis* and *trans* triplet states of the dienes in different relative amounts. This hypothesis still seems sound and is consistent with the fact that all sensitizers give the same distribution of products in the dimerization of cyclopentadiene. Sensitizers having large triplet excitation energies, *e.g.*, benzophenone, acetophenone, and Michler's ketone, all give the same results and we presume that such sensitizers produce mainly *trans* triplets which react with dienes to give relatively large amounts of cyclobutane derivatives. Details of energy transfer involving low energy sensitizers, some of which give large yields of *trans* triplets and, consequently, large yields of cyclobutanes are complicated[18a] and still the subject of study in our laboratory. Extensive discus-

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[16] P. E. Eaton, *J. Am. Chem. Soc.*, **84**, 2344 (1962).

[17] Probably all fractions contain an inseparable mixture of stereoisomers. See Experimental for details.

[18] (a) See, for example, J. Saltiel and G. S. Hammond, *J. Am. Chem. Soc.*, **85**, 2515, 2516 (1963), for a discussion of related problems; (b) D. J. Trecker, R. L. Brandon, and J. P. Henry, *Chem. Ind. (London)*, 652 (1963).

sion at this time would be premature. For practical purposes, benzophenone and 2,3-pentanedione can be recommended as likely to give both acceptable rates of reaction and near maximum variation of product distribution.

Trecker, Brandon, and Henry[18b] recently have reported photodimerization of isoprene using benzil as the sensitizer. Although their results are similar to ours, there are important differences. They did not find compound **6**, which we find as a minor constituent in all mixtures; in addition, they reported that **11** is a photoproduct. We find that **11** is absent from mixtures that are analyzed using minimum temperature of the inlet to the v.p.c. apparatus although **5** does undergo rather facile thermal rearrangement to **11**. The presence of **6** implies that triplet isoprene is not well represented by the localized structure suggested by Trecker, *et al.* The same conclusion is implicit in our explanation of the effects of various sensitizers.[5]

Experimental

Materials.—Butadiene, Matheson Coleman and Bell instrument grade, was used directly for preparative dimerizations. The diene was purified by preparative v.p.c. on the Megachrom apparatus for use in the study of various effects on the relative yields of dimers. This procedure eliminated the necessity of correcting for the small amount of 4-vinylcyclohexene in the butadiene.

Cyclopentadiene was prepared immediately before use by cracking dicyclopentadiene, Matheson Coleman and Bell practical grade, at 172°. The fraction boiling at 40–42° was collected for use.

1,3-Cyclohexadiene (Columbia or Aldrich reagent grade) was distilled and the fraction boiling at 80–82° was collected for immediate use.

Isoprene (Phillips Petroleum Company pure grade) was distilled and the fraction boiling at 33.0° was collected for use.

Piperylene (Matheson Coleman and Bell technical grade, a mixture of the stereoisomers) was distilled and the fraction boiling at 42.0° was collected for use.

2,3-Dimethylbutadiene (Columbia Chemicals) was distilled and the fraction boiling at 68.5–70.0° was used.

Sensitizers were all reagent grade or the best quality commercially available.

Vapor chromatographic analyses were made on either a Loenco Model 15 or an Aerograph chromatograph.

Preparative Dimerizations and Characterization of Products. Dimerization of 1,3-Butadiene.—1,3-Butadiene (80–100 g.) was irradiated in a Hanovia Type S 200-watt immersion apparatus equipped with a 2800-Å. cutoff filter. The lamp housing was cooled with ethylene glycol–ice–water and the entire reactor was surrounded by a 1-gal. dewar flask filled with Dry Ice. The sensitizer (5–15 g.) was added and the solution irradiated. The course of the reaction was followed by periodic sampling and analysis by v.p.c. at 75° employing a 6 ft. by 1/4 in. column packed with 35% Carbowax 20M. Three new peaks, 1, 2, and 3, appeared in the vapor chromatograms. In the presence of 2,3-pentanedione, for example, the reaction went to near completion in about 80 hr., while the reaction was only 12% complete at 40 hr. in the presence of benzophenone or acetophenone. The following is a typical work-up procedure. Eighty milliliters of 1,3-butadiene containing 15 ml. of 2,3-pentanedione was irradiated for 80 hr. at which time only 4% unchanged butadiene remained, as indicated by v.p.c. analysis. The diketone was removed by passage of the mixture through an alumina column and the eluent heated under reflux at 120° for 3 hr. to convert *cis*-1,2-divinylcyclobutane to *cis,cis*-1,5-cyclooctadiene (*vide infra*). The resulting mixture was then fractionated through a spinning-band column. The fractions obtained were 15 g. of *trans*-1,2-divinylcyclobutane, b.p. 111–113°, n^{25}D 1.4430; 12 g. of 4-vinylcyclohexene, b.p. 128°, n^{25}D 1.4620; and 2 g. of *cis, cis*-1,5-cyclooctadiene, b.p. 150–155°, n^{25}D 1.4930.

An alternate procedure for preparing *trans*-1,2-divinylcyclobutane was found more convenient than the previous procedure. Butadiene (37 g.) saturated with Michler's ketone (*p,p'*-tetramethylaminobenzophenone) was added to a constricted 25 × 200 mm. Pyrex test tube, frozen, degassed, and sealed under vacuum. The tube was irradiated for 50 hr. with a 450-watt Hanovia arc provided with a Pyrex housing. The entire system was maintained below 30° by a water bath. The irradiated sample was heated at reflux for 30 min. to convert the *cis*-1,2-divinylcyclobutane to *cis,cis*-1,5-cyclooctadiene and then fractionated through a spinning-band column as described previously. *trans*-1,2-Divinylcyclobutane (19 g.) in greater than 95–96% purity was obtained.

Rearrangement of *cis*-1,2-Divinylcyclobutane.—Pure *cis*-1,2-divinylcyclobutane was obtained by preparative vapor chromatography on Carbowax. Twenty milligrams of the pure material was heated in a sealed tube for 18 hr. at 120°. Analysis by v.p.c. of the reaction product showed that the starting material was completely gone and only one new peak appeared in the trace. The infrared spectrum, boiling point, and index of refraction of this compound agreed exactly with those reported in the literature for *cis,cis*-1,5-cyclooctadiene.

Ozonolysis of *trans*-1,2-Divinylcyclobutane.—Two grams of the diene was dissolved in 100 ml. of ethyl acetate and ozonized for 6 hr. at −78°. The ozonide was decomposed by adding a solution prepared from 6 ml. of 30% hydrogen peroxide and 80 ml. of water followed by heating of the resultant solution on a steam bath for several hours. Upon concentration and cooling, an oil formed. The oil was extracted with ether, the extract dried, and then concentrated to yield yellow crystals. After two recrystallizations from benzene–ethyl acetate, white crystals of *trans*-cyclobutanedicarboxylic acid, m.p. 127° (lit. 129°), were obtained.

Anal. Calcd. for $C_6H_8O_4$: neut. equiv., 72. Found: neut. equiv., 68 and 75.

Dimerization of Isoprene.—In a typical run eight narrow necked test tubes (Kimax 120 × 115 mm.) were filled with a solution of 10 g. of benzophenone in 80.8 g. (115 ml.) of isoprene. The solution was then degassed and the tubes sealed *in vacuo*. They were irradiated for 5 days with a 250-watt Hanovia mercury lamp with a filter having a 2800-Å. cutoff. V.p.c. analysis of the irradiated solution showed 65% conversion. Analytical vapor chromatography shows the following relative amounts of products: **4**, 29%; **5**, 30%; **6**, 5%; **7**, 9%; **8**, 2%; **9**, and **10**, 18%. The contents of the tubes were combined and vacuum distilled. The fraction boiling at 40–60° (1–5 mm.) contained all the dimers. Preparative v.p.c. was used for complete separation of the dimers. The distillate was first passed through a Carbowax column, which separated the seven dimers into five fractions.

The first fraction contained purely the lowest boiling dimer, which was identified as *trans*-**1,2-dimethyl-1,2-divinylcyclobutane** (**4**). **4** has the following properties: b.p. 134.5–135.0° (744 mm.); $n^{27.0}$D 1.4541; infrared absorption: 3.24 (s), 3.38 (s), 3.48 (s), 3.50 (s), 5.50 (w), 6.10 (s), 6.91 (s), 7.10 (s), 7.30 (s), 7.88 (w), 8.20 (w), 9.24 (s), 9.55 (w), 10.1 (s), 11.0 (s), 13.7 (s) μ; n.m.r. absorption: 0.85 (methyl protons), 1.0–2.4 (complex 14 peak band system of 4 methylene protons), 4.5–4.9 (complex band system of four terminal ethylenic protons), 5.4–6.0 p.p.m. (complex band system of two nonterminal ethylenic protons).

Anal. Calcd. for $C_{10}H_{16}$: C, 88.16; H, 11.84. Found: C, 87.77; H, 11.90.

The second fraction was also homogeneous. It is *trans*-**1-isopropenyl-2-methyl-2-vinylcyclobutane** (**5**), b.p. 152.5–153.0° (744 mm.); $n^{27.0}$D 1.4591; infrared absorption: 3.24 (s), 3.38 (s), 3.50 (s), 6.06 (s), 6.91 (s), 7.08 (m), 7.28 (s), 8.05 (m), 8.96 (w), 9.62 (m), 10.05 (s), 11.2 (s), 14.6 (m), μ; n.m.r. spectrum: 0.80 (tertiary methyl), 1.36 (vinyl methyl), 1.0–2.2 (complex band system of four methylene protons), 2.3–2.8 (nonsymmetrical triplet of tertiary proton), 4.3–4.9 (complex band system of four terminal vinyl protons), 5.5–6.1 p.p.m. (four lines of increasing intensity as going upfield, nonterminal ethylenic proton).

Anal. Found for **5**: C, 87.82; H, 11.88.

The third fraction contained two dimers (**6** and **7**). A 6-ft. Apiezon J column was used to separate the two. The first to emerge from the Apiezon column was shown to be *trans*-**1,2-diisopropenylcyclobutane** (**6**), b.p. 155.1–155.4° (740.0 mm.); $n^{29.0}$D, 1.4585; infrared absorption: 3.24 (s), 3.37 (s), 5.90 (m), 6.06 (s), 6.88 (s), 7.26 (s), 7.88 (m), 7.98 (m), 11.3 (s) μ; n.m.r. spectrum (internally aligned with tetramethylsilane): 1.65 (methyl protons, signal overlaps with methylene signal), 1.7–2.5 (complex band system of four methylene protons), 2.5–2.9

(five peaks band system of two tertiary protons), 4.67 p.p.m. (terminal ethylenic protons).

Anal. Found for **6**: C, 87.66; H, 11.95.

The second compound in the third fraction was shown to be **1,4-dimethyl-4-vinyl-1-cyclohexene** (**7**), b.p. 160.5–161.5° (741.0 mm.); $n^{27.8}$D 1.4658; infrared absorption: 3.24 (m), 3.32 (m), 3.33 (m), 3.38 (s), 3.42 (s), 3.50 (s), 6.10 (m), 6.92 (w), 7.08 (m), 7.28 (m), 7.61 (w), 8.25 (w), 8.65 (w), 9.42 (m), 9.76 (w), 10.0 (s), 10.5 (w), 10.6 (w), 11.0 (s), 12.5 (m), 13.1 (w), 13.9 (w) μ; n.m.r. spectrum: 1.00 (tertiary methyl), 1.69 (allylic methyl, overlapping with methylene protons), 1.25–2.2 (complex band system of methylene protons), 4.6–5.1 (complex band system of $=CH_2$, 5.05 (ethylenic protons on the ring), 5.5–6.1 p.p.m. (four lines of increasing intensity going upfield, nonterminal ethylenic proton).

Anal: Found for **7**: C, 87.39; H, 11.96.

The fourth fraction was homogeneous. The physical properties agree with those of an authentic sample of dipentene (*d,l*-limonene).

The last fraction appeared homogeneous at first, but when a sample was passed through a 12 ft. × $^1/_4$ in. column packed with 25% β,β'-oxydipropionitrile two peaks appeared on the chromatograph. The separation was not complete; the isolated sample of **9** was found 70% pure. This was the minor component in the mixture. The sample of dimer **10** was at least 90% pure (based on relative intensities of infrared absorptions at 9.35 and 9.15 μ). By comparison with the second product of the thermal rearrangement of **5**,**9** was assigned the structure, **1,5-dimethyl-1,5-cyclooctadiene**, b.p. 182.4° (741.0 mm.); $n^{28.2}$D 1.4863; infrared absorption: 3.39–3.50 (s), 6.71 (m), 6.92 (s), 7.28 (m), 7.94 (w), 8.20 (w), 8.72 (w), 9.38, (m), 9.78 (w), 10.1 (m), 10.4 (w), 11.1 (w), 11.6 (m), 12.0 (s), 12.4 (w) μ; n.m.r. spectrum: 1.66 (methyl protons), 2.28 (methylene protons), 5.27 p.p.m. (ethylenic protons) (internally aligned with tetramethylsilane). **10** was assigned the structure **2,5-dimethyl-1,5-cyclooctadiene**; infrared absorption: 3.38–3.50 (s), 6.70 (m), 6.92 (s), 7.28 (m), 7.95 (w), 8.20 (w), 8.63 (w), 9.15 (m), 9.70 (w), 10.1 (w), 10.6 (w), 11.1 (w), 11.6 (m), 12.0 (s), 12.4 (w) μ; n.m.r. spectrum: 1.66 (methyl protons), 2.25 (methylene protons), 5.27 p.p.m. (vinyl protons) (tetramethylsilane as internal standard); b.p. 182.5–184.0° (744.0 mm.); n^{27}D 1.4870.

Anal. Found for fraction 5 (35% **9** and 65% **10**): C, 87.36; H, 11.94.

Rearrangement of *trans*-1,2-Dimethyl-1,2-divinylcyclobutane.—Consecutive readings of the boiling point (micro boiling point method) showed that under reflux, the boiling point of a sample of **4** rose steadily from 135° to a constant value of 161° within half an hour. Therefore, in a preparative run, 2 ml. of **4** was refluxed for half an hour. The two products were separated on a Carbowax column. The lower boiling product is in every respect identical with **7** while the retention time on a β,β'-oxydipropionitrile column of the high boiling product agrees with that of **10**.

Anal. Found for first rearranged product, **7**: C, 87.94; H, 11.59.

Rearrangement of *trans*-1-Isopropenyl-2-methyl-2-vinylcyclobutane.—By a procedure similar to that described previously, **5** was found to rearrange completely during 3.5 hr. at the reflux temperature. Separation of products also was carried out on a Carbowax column. There were three rearranged products. The lowest boiling one had the following physical properties: b.p. 160.3° (741.0 mm.); $n^{28.5}$D 1.4620; infrared absorption: 3.24 (m), 3.28 (m), 3.38 (s), 3.42 (s), 3.50 (s), 6.10 (m), 6.92 (s), 7.08 (m), 7.28 (m), 7.42 (w), 8.25 (w), 8.88 (w), 8.98 (w), 9.08 (w), 9.60 (w), 10.0 (s), 10.6 (w), 11.0 (s), 12.1 (w), 12.5 (s), 13.8 (w) μ; n.m.r. spectrum: 1.00 (tertiary methyl), 1.67 (allylic methyl, overlapping with methylene protons), 1.25–2.2 (complex band system of methylene protons, its structure being definitely different from that of **7**), 4.6–5.1 (band system of terminal vinyl), 5.05 (vinyl proton on the ring), 5.5–6.1 p.p.m. (four lines of increasing intensity going upfield, nonterminal vinyl proton). It has been assigned the structure, **2,4-dimethyl-4-vinyl-1-cyclohexene** (**11**).

Anal. Found for **11**: C, 88.12; H, 11.67.

The second rearranged product is in all respects identical with *d,l*-limonene.

Anal. Found for second rearranged product: C, 88.10; H, 11.88.

The third rearrangement product is identical with **9**.

Anal. Found for third rearranged product: C, 88.28; H, 11.69.

Dimerization of Piperylenes.—A solution of 300 ml. of distilled piperylenes with 0.04 mole % of benzophenone was irradiated for 7 days in a Hanovia type S 200-watt immersion apparatus equipped with 2800-Å. cutoff filter and a reflux condenser. V.p.c. analysis on a Carbowax column of the reaction mixture showed approximately 60% conversion to new products with the appearance of 15 new peaks on the chromatograph. The mixture of new products was collected by vacuum distillation (35–60° at 2–5 mm.), and separated by preparative v.p.c. technique on a Carbowax column, collecting only the three major products (**16**, **17**, and **18**). Analytical vapor chromatography showed that these compounds represented 52%, 22%, and 8%, respectively, of the dimeric products.

Compound **16** was assigned the gross structure of ***trans*-1,2-cyclobutane**, and has the following properties: b.p. 159.5° (744 mm.); infrared absorption: 3.33 (s), 3.35 (s), 3.45 (s), 3.50 (s), 5.89 (w), 6.00 (w), 6.04 (w), 6.90 (s), 6.95 (s), 7.10 (m), 7.26 (m), 7.68 (w), 7.90 (w), 8.10 (w), 9.00 (w), 9.65 (w), 10.4 (s), 10.6 (m), 10.8 (w), 11.0 (w), 14.2 (s) μ. Absorption at 10.4 μ is characteristic for a *trans* disubstituted double bond, while 14.2 μ is characteristic for the *cis*[18] configuration. This can be interpreted as indicating that **16** contains one propenyl group bearing *trans* substituents and the other having *cis* substituents, or that **16** is a mixture of three isomers. The n.m.r. spectrum shows (1) a complicated group of peaks between 1.6 and 2.3 p.p.m. assigned to six methyl protons and four methylene protons, (2) a broad band between 2.4 and 3.4 p.p.m. due to two tertiary protons, and (3) a complicated group of peaks between 5.3 and 6.0 p.p.m. assigned to the four vinyl protons. Relative ratio of integrated areas of the three groups is 9.92:2.00:3.90. The two propenyl groups are probably *trans* to each other because of the stability of **16**.

Compound **17** has the following properties: b.p. 145.8–146.0° (744 mm.); infrared absorption: 3.25 (s), 3.33 (s), 3.38 (s), 3.45 (s), 3.50 (s), 5.48 (w), 6.10, (s), 6.89 (s), 7.03 (w), 7.10 (m), 7.26 (m), 7.50 (w), 7.61 (w), 7.71 (w), 7.90 (w), 8.07 (w), 8.85 (m), 10.1 (s), 10.4 (s), 11.0 (s), 12.0 (w), 14.0 (s) μ. Absorption at 10.4 and 14.0 μ shows the presence of both *trans* and *cis* disubstituted double bonds. The n.m.r. spectrum shows (1) an unsymmetrical doublet at 1.05 and 1.15 p.p.m. assigned to three methyl protons (the doublet is attributed to the presence of unequal amount of isomers of different orientation of methyl group in the ring); (2) a complicated group of peaks between 1.6 and 3.2 p.p.m., corresponding to eight protons, three methyl protons, two methylene, and three tertiary protons; and (3) a complicated group of peaks between 4.9–6.2 p.p.m. attributed to five vinyl protons. Integrated ratio of high field proton to vinyl proton is 11.4:5.00. The spectrum appears to be consistent with the gross structure of **1-methyl-2-vinyl-3-propenylcyclobutane**, with the vinyl and propenyl group probably *trans* to each other.

Compound **18** has infrared absorption maxima at 3.25 (s), 3.35 (s), 3.38 (s), 3.40 (s), 3.46 (s), 3.51 (s), 5.59 (w), 5.77 (w), 6.11 (s), 6.88 (s), 7.02 (m), 7.08 (m), 7.30 (m), 7.55 (m), 7.73 (w), 8.15 (w), 8.28 (w), 8.68 (w), 8.82 (w), 9.00 (w), 9.18 (w), 9.52 (w), 10.7 (m), 11.0 (s), 11.5 (m), 12.2 (w), 13.7 (m) μ; n.m.r. absorption at (1) an unsymmetrical doublet at 1.1–1.2 p.p.m. assigned to methyl groups of different isomers, (2) a group of peaks between 1.5 and 2.3 p.p.m. assigned to four tertiary protons, (3) a group of lines between 4.9 and 5.4 p.p.m. due to four terminal vinyl protons, and (4) a group of peaks between 5.6 and 6.0 p.p.m. assigned to two nonterminal vinyl protons. Integration is consistent with the assignment. **18** is, therefore, assigned the gross skeletal structure of **1,2-dimethyl-3,4-divinylcyclobutane**, with the vinyl groups probably *trans* to each other.

Dimerization of Cyclopentadiene.—In a typical run 10–20 g. of sensitizer was added to 140 g. of freshly cracked cyclopentadiene, and the resulting solution was irradiated in a Hanovia 450-watt immersion apparatus cooled in a similar manner to that described previously for dimerizations of butadiene. The temperature of the reaction mixture was maintained at −10° or lower in order to minimize the thermal dimerization. The reaction was usually complete after 24 hr. of irradiation as shown by disappearance of monomer in the v.p.c. analysis. The reaction mixture was distilled under vacuum yielding 130 g. of material boiling at 32–40° (1–2 mm.). V.p.c. analysis on a 12 ft. × 1/4 in. β,β'-oxydipropionitrile column showed that the products were eluted as three peaks practically equal in area (after corrections

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(19) See, *e.g.*, L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1962, pp. 45-48.

for the thermal dimerization). Freshly distilled dimers were separated into two fractions at 90° by preparative v.p.c. on a Megachrom apparatus, equipped with eight 6 ft. × 5/8 in. columns packed with 35% Apiezon J. The two separated fractions consisted of a mixture of two stereoisomers, *exo*-dicyclopentadiene (**13**) and *endo*-dicyclopentadiene (**12**), and pure *trans*-tricyclo$[5.3.0.0^{2,6}]$-3,9-decadiene (**14**). The two stereoisomers were separated by preparative v.p.c. employing a single 6 ft. × $^5/_8$ in. β,β'-oxydipropionitrile column in the Megachrom. The *endo*-dicyclopentadiene produced in the photodimerization had b.p. 170–172°, $n^{25}\text{D}$ 1.5080, and infrared and n.m.r. spectra identical with those of an authentic sample prepared by the method of Bartlett and Goldstein.[15] *trans*-Tricyclo$[5.3.0.0^{2,6}]$-3,9-decadiene had b.p. 170–172°, $n^{25}\text{D}$ 1.5080.

Hydrogenation of *trans*-Tricyclo$[5.3.0.0^{2,6}]$-3,9-decadiene 14.—A 0.5-g. sample of the dimer, **14**, contaminated with about 20% of *endo*-dicyclopentadiene was dissolved in 5 ml. of 95% ethanol and then placed in a 25-ml. hydrogenation flask. Platinum dioxide (50 mg.) was added and the mixture was treated with hydrogen gas (uptake 170 ml.). The mixture was then filtered and concentrated. Analysis by v.p.c. on a β,β'-oxydipropionitrile column at 80° showed that the diene had been completely converted and a compound of considerably shorter retention time was detected. This compound was obtained pure by preparative v.p.c. The material did not decolorize a solution of bromine in carbon tetrachloride or an aqueous solution of potassium permanganate. The infrared and n.m.r. spectra of the saturated material were identical with those of the hydrocarbon produced by Wolff-Kischner reduction of *trans*-tricyclo$[5.3.0.0^{2,6}]$-3,8-decanedione.[16]

***trans*-Ditosyloxytricyclo$[5.3.0.0^{2,6}]$-3,8-decane.**—Tricyclo-$[5.3.0.0^{2,6}]$-3,8-decanedione was prepared by the method of Eaton.[16] A 10.0-g. sample was dissolved in 250 ml. of 95% ethanol and cooled in an ice bath. A solution of 5.0 g. of sodium borohydride in 20 ml. of 0.1 *N* aqueous sodium hydroxide was then added slowly. An exothermic reaction occurred and the mixture became cloudy. After 2 hr. of stirring with cooling, the mixture was concentrated to 50 ml. and diluted with 20 ml. of cold water. The alcohol was exhaustively extracted with ether and methylene chloride. The extracts were combined, dried, and concentrated until crystals appeared. The crystals were filtered and dried; m.p. 193–194°; yield, 8.0 g.

Anal. Calcd. for $C_{10}H_{16}O_2$: C, 71.50; H, 9.54. Found: C, 71.88; H, 9.66.

The spectrum of a potassium bromide pellet showed a broad alcohol band at 3200 cm.$^{-1}$. The diol (1.0 g.) was dissolved in pyridine (15 ml.) and cooled in an ice bath. A solution of 3.0 g. of tosyl chloride dissolved in 15 ml. of pyridine was added to the stirred solution. After 5 hr. of stirring the mixture was left overnight in the refrigerator. The mixture was then poured into cold 1 *N* sulfuric acid and crystals appeared. The crystals were washed with pentane and then recrystallized from hexane; m.p. 158–159° dec.; yield, 1.8 g.

Anal. Calcd. for $C_{24}H_{28}S_2O_6$: C, 60.50; H, 5.92; S, 13.43. Found: C, 59.44; H, 5.88; S, 13.54.

***trans*-Tricyclo$[5.3.0.0^{2,6}]$-3,8-decadiene** (**15**).—Potassium was dissolved in freshly distilled *t*-butyl alcohol (20 ml.) under nitrogen. A 1.5-g. sample of the tosylate was added slowly to the solution and the mixture was heated under reflux overnight. Cold water (100 ml.) was added to the cooled solution. The mixture was filtered and the aqueous filtrate was extracted three times with pentane. The extract was dried and concentrated to yield 80 mg. of product. The product was obtained pure by preparative vapor chromatography on a β,β'-oxydipropionitrile column. The pure material had a retention time longer than that of the tricyclodiene produced in the photoreaction and could be separated from the latter.

***trans*-Ditosyloxytricyclo$[5,3,0,0^{2,6}]$-3,9-decane.**—Tricyclo-$[5.3.0.0^{2,6}]$-3,9-decanedione was separated from the mixture of cyclopentenone photodimers according to the method of Eaton[16] and reduced with sodium borohydride by the procedure described previously for the preparation of the isomeric diol. The diol was purified by continuous extraction with ether in a Soxhlet apparatus; m.p. 168–170°.

Anal. Calcd. for $C_{10}H_{18}O_2$: C, 71.50; H, 9.54. Found: C, 71.16; H, 9.68.

The tosylate of this diol was prepared as described previously. The crude tosylate was extracted three times with benzene and then recrystallized from hexane; m.p. 119–120°.

Anal. Calcd. for $C_{24}H_{28}S_2O_6$: C, 60.50; H, 5.88; S, 13.43. Found: C, 60.58; H, 6.12; S, 12.60.

***trans*-Tricyclo$[5.3.0.0^{2,6}]$-3,9-decadiene** (**14**).—Four grams of the tosylate was added to a refluxing solution of 4 g. of potassium in 35 ml. of *t*-butyl alcohol (under nitrogen). The mixture was analyzed after 5 hr. by v.p.c. on a β,β'-oxydipropionitrile column and a product was found with retention time identical with that of the tricyclodecadiene produced in the photodimerization of cyclopentadiene. The yield calculated from the v.p.c. data was 0.6 g. The material was obtained pure by preparative chromatography on a β,β'-oxydipropionitrile column. It possessed infrared and n.m.r. spectra identical with those of the tricyclic dimer.

The Reaction of Benzenesulfonyl Azide with Bicyclo[2.2.1]-2-heptene

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Received April 15, 1963

Benzenesulfonyl azide has been found to react with bicyclo[2.2.1]-2-heptene at room temperature in an inert solvent to give a product II, in excellent yield, arising from the addition of the azide to the alkene followed by loss of molecular nitrogen. The nitrogen-containing ring of II was readily opened with hydrogen bromide, hydrogen chloride, acetic acid, and neutral, acidic, and alkaline aqueous solutions to give 7-benzenesulfonamidobicyclo[2.2.1]heptane derivatives. N-Acetyl, chloroacetyl, and benzenesulfonyl derivatives of 7-aminobicyclo-[2.2.1]heptane prepared from II were shown not to be identical with similar derivatives of 2-*exo*- and 2-*endo*-aminobicyclo[2.2.1]heptane by melting point, infrared spectra, and thin layer and gas chromatography. Two possible structures, the aziridine A and the azetidine C, are consistent with the chemical data. The azetidine structure C is suggested for the product on the basis of n.m.r. comparisons and base-catalyzed opening of the nitrogen-containing ring ultimately to yield 7-aminobicyclo[2.2.1]heptane.

Over fifty years ago phenyl azide was reported to react with acetylene to give 1-phenyltriazole, on heating the reactants in an acetone solution in a sealed tube at 100° for 20 hr.[3] Later it was found that bicyclo-[2.2.1]-2-heptene and its derivatives react with phenyl azide in the cold to form triazolines which usually crystallized from the solution after only a few minutes.[4] Since only strained alkenes were found to react readily with phenyl azide, the reaction soon became a diagnostic test for angular strain in double bonds. Recently, Huisgen and his associates[5] have found that this reac-

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